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Electron-Acceptor Nanomaterials Fabricated by Electrospinning for Polymer Solar Cells

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Abstract

Nanofibers of a fullerene derivative (phenyl-C_{61}-butyric acid methyl ester, PCBM) and a conventional polymer (polyvinylpyrrolidone, PVP) composite were prepared by electrospinning of blended solutions in the mixed solvent of chlorobenzene and methanol. At a fixed concentration of PVP, the average diameter of fibers was found to decrease with increasing composition of PCBM, because of the increase of conductivity of spinning solutions. The increase in PCBM composition resulted in a relative blue shift in UV-vis absorption peak. PVP was easily removed from PCBM/PVP fibers by Soxhlet extraction. After the removal of PVP, pure PCBM were obtained as nanorods connected in fiber direction. The preliminary utilization of the PCBM nanostructure as an electron-acceptor material in polymer solar cells was investigated.

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Keyword: Nanostructures; fullerene; electrospinning; polymer solar cells

1. Introduction

Nanostructures have been interested recently because when the diameters of conventional materials are shrunk to nanometer scales, several specific characteristics, such as flexibility in surface functionalities, very large surface area to volume ratio, and improved mechanical performance, will appear [1].

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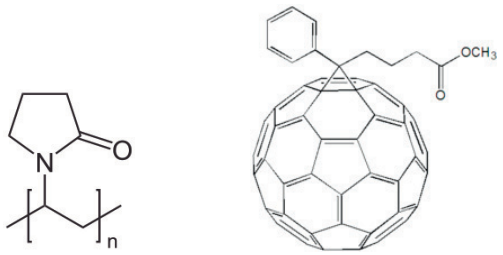
Electrospinning is one of nanostructure-fabrication techniques which become a simple technique that uses electrostatic forces to produce polymeric, ceramics, and composite fibers with diameters ranging from microns down to nanometers.

Now a day, charge conducting nanomaterials are being exploited in many applications because of a combination of optical and electronic properties [2]. We have previously reported the fabrications of hole-conducting one-dimensional nanomaterials by electrospinning, especially nanofibers made of conducting polymers [3-6]. Derivatives of poly(*p*-phenylene-vinylene) [3-5] and polythiophene [6] were blended with conventional (insulating) polymers, such as polystyrene (PS) or PVP [see chemical structure of PVP in Fig. 1(a)], in the proper solvents. The solutions could be electrospun to form ultrafine conducting polymer/insulating polymer composite fibers. Typically, PVP could be removed from the composite fibers by selective extractions. The obtained conducting polymer nanofibers were also utilized as the electron donor material in bulk-heterojunction polymer solar cells [7].

Not only hole conducting materials, a number of researchers also reported the fabrication of electron conducting nanofibers. Various metal nanofibers were also successfully fabricated by electrospinning [8-9]. However, they are not utilized as the electron acceptor materials in polymer solar cells. More conventional materials that were extremely used as the electron acceptor material in polymer solar cells are fullerene and its derivatives. To increase the power conversion efficiency in polymer solar cells, the connection of the electron acceptor material with high surface area is very important.



(a) (b)

Fig. 1. Chemical structures of (a) PVP and (b) PCBM.

In the present contribution, electrospinning was used to fabricate connected phase of a derivative of fullerene, i.e. PCBM [see its chemical structure in Fig. 1(b)]. Electrospinning of PCBM in its blends with PVP, an easily spinnable and easily extractable polymer, in mixed solvent of chlorobenzene and methanol was carried out. Ultraviolet-visible (UV-vis) absorption was investigated. The preliminary utilization of the PCBM nanostructure as an electron-acceptor material in polymer solar cells was also investigated.

2. Experimental

2.1. Chemicals

PCBM was purchased from American Dye Source and PVP (M_w = 1,300,000) powders was purchased from Aldrich. The solvent used was the mixture of chlorobenzene and methanol (Wako).

2.2. Electrospinning and Characterizations

Solutions of PCBM were prepared in chloro-benzene/methanol (85:15 v/v) under vigorously stirring. A controlled amount of PVP (corresponding to the fixed concentration of 6% w/v) was added into PCBM solutions with vigorously stirring. The composition ratio of PCBM to PVP was varied as 1:3, 2:3, and 3:3.

Prepared solutions were loaded in a 3-ml plastic syringe. The nozzle was a blunt-end stainless-steel gauge 22 needle. The collector was a sheet of aluminum foil on a plastic plate. A Gamma High Voltage Research power supply was used to charge the solution across an electrode in solution and the collector. As-prepared solutions were electrospun under an applied electrical potential of 15 kV over a fixed collection distance of 15 cm at room temperature. The solution feed rate was controlled by means of Kd Scientific syringe pump at 1 $mL \cdot h^{-1}$. The collection time were fixed for all experiments at 1 min. For the removal of PVP from as-spun PCBM/PVP fibers, the Soxhlet extraction was carried out. Methanol was used as a solvent at the extraction temperature of 75˚C. The extraction time was fixed at 12 h. The samples were then dried overnight at 60 ˚C in a vacuum oven. The morphological appearance of the as-spun fiber mats was investigated by a JEOL JSM-6500FE scanning electron microscope (SEM). UV-vis spectra were measured by a Shimadzu UV-2450 UV-vis spectrophotometer.

2.3. Photovoltaic Device Fabrications and Characterizations

The photovoltaic cells were prepared on glass/ITO substrates. The substrates were cleaned in an ultrasonic bath with water and acetone. A layer of TiO_2 film was fabricated by spin-coating of TiO_2 precusor. The solution of PCBM/PVP was then deposited by electrospinning. PVP was removed by Soxhlet extraction. Poly(3-hexylthiophene-2,5-diyl) (P3HT) was then deposited by spin-coating. Finally, an Au electrodes were deposited by evaporation. The current density-voltage (*J-V*) characteristics of the obtained cells were measured under simulated solar light (AM 1.5, 100 mW/cm^2).

3. Results and Discussion

Figure 2 (with suffix 1) shows the SEM images of electrospun fibers from PCBM/PVP blended solutions at composition ratios of PCBM to PVP of 1:3, 2:3, and 3:3, where the concentration of PVP was fixed at 6% w/v. It was found that electrospinning of blended solutions resulted in ultrafine PCBM/PVP composite fibers with the average diameters ranging in sub-micrometers. The average diameter of fibers was found to decrease with increasing composition of PCBM (from ~3 to ~1.7 μm). Investigation by conductivity tester found that the conductivity of spinning solutions increased with increasing composition of PCBM. This result corresponds to the decrease of diameter of fibers with increasing composition of PCBM due to increasing electrostatic force during the electrospinning.

Figure 3 shows UV-vis spectra of as-spun PCBM/PVP fibers at various blending ratios of PCBM to PVP with an inset that shows the corresponding spectra emphasized the peak positions. It was found that the increase in PCBM composition resulted in a relative blue shift in UV-vis absorption peak. This can be attributed to more connection of the PCBM in the electrospun fibers with increasing PCBM composition.

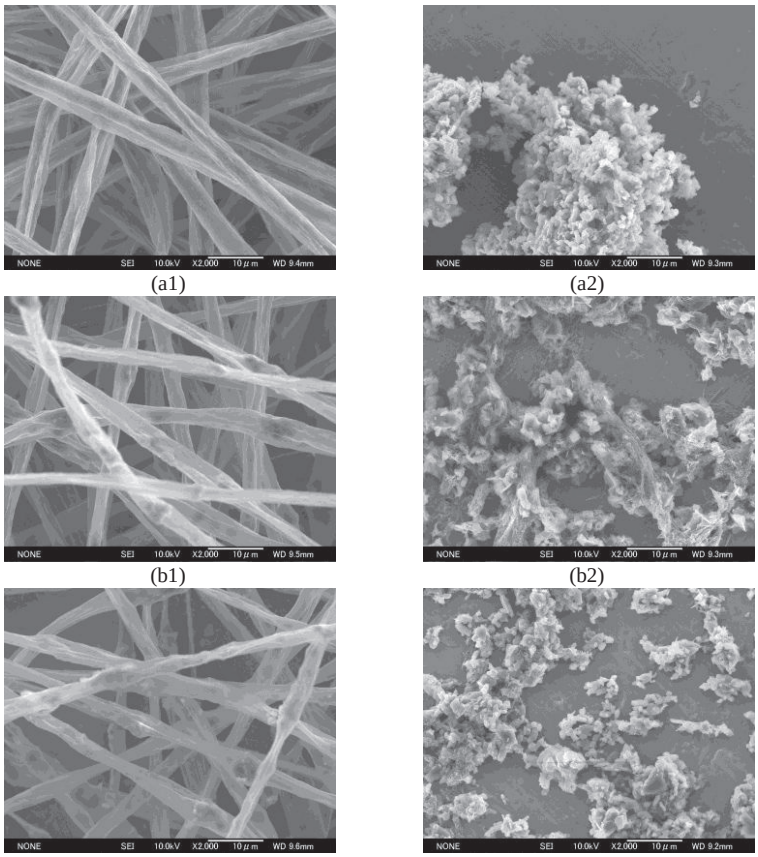


Fig. 2. SEM images of electrospun fibers from PCBM/PVP blended solutions in mixed solvent of chlorobenzene and methanol (85:15 v/v) at blending ratios of PCBM to PVP of (a) 1:3, (b) 2:3, and (c) 3:3. The concentration of PVP was fixed at 6% w/v. Suffixes "1" and "2" represent before and after the removal of PVP by the Soxhlet extraction, respectively.

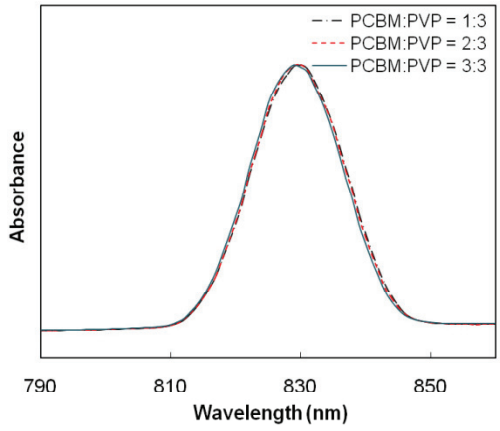


Fig. 3. Normalized UV-vis spectra of as-spun PCBM/PVP fibers at various blending ratios of PCBM to PVP. Inset is the corresponding spectra emphasized the peak positions.

After the removal of PVP from as-spun fibers by Soxhlet extraction, pure PCBM fibers were obtained as nanorods connected in fiber direction. The higher composition of PCBM, the higher PCBM-connected phase. This result totally corresponds to other evidences reported in the previous texts.

Obtained structures and properties of PCBM nanomaterials may be widely applied to somes specific applications. In this step, nanofibers have been applied to an electron acceptor layer of polymer solar cells without any thermal post-treatment. By combination of these electrospun PCBM nanorods with the P3HT, it is possible to fabricate bulk-heterojunction organic photovoltaic cells (structure: ITO / TiO_2 / PCBM nanomaterial / P3HT / Au).

Table 1 shows the photovoltaic properties of the cells investigated, including photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (*FF*), and power conversion efficiency. It was found that the power conversion efficiency of the cell investigated was acceptable with the value of 0.34%. To increase the power conversion efficiency, the increase of photovoltaic properties, espectially *FF*, is very important. The reduction of the diameter of fibers to increase the surface area of obtained fibers is a recommended method and this ettemp is under way.

Table 1. An example of a table

Photovoltaic Properties	Value
J_{sc} (mA/cm^2)	2.22
V_{oc} (V)	0.57
FF	0.26
Power Conversion Efficiency (%)	0.34

4. Conclusions

Nanofibers of PCBM/PVP composite were prepared by electrospinning of blended solutions in the mixed solvent of chlorobenzene and methanol. At a fixed concentration of PVP of 6% w/v, the average diameter of fibers was found to decrease with increasing concentration of PCBM, because of the increase of conductivity of spinning solutions. The increase in PCBM composition resulted in a relative blue shift in UV-vis absorption peak. After the removal of PVP, pure PCBM were obtained as nanorods connected in fiber direction. The preliminary utilization of the PCBM nanostructure as an electron-donor material in polymer solar cells showed a relatively acceptable power conversion efficiency of 0.34%.

Acknowledgements

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